PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-325195
(43)Date of publication of application : 10.12.1996

(51)Int.Cl. C07C 61/00
C01B 31/02
C04B 41/88
C07C205/05
C07C303/04

(21)Application number : 07-170098
(22)Date of filing : 31.05.1995

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(54) METAL-COATED CARBON NANOTUBE AND ITS PRODUCTION

(57)Abstract:
PURPOSE: To produce carbon nanotube whose surface is coated with a metal.
CONSTITUTION: An ion containing a metal is deposited as a metal or a metal salt utilizing a chemical reaction such as an ion exchange reaction, an oxygenphilic reaction or a reduction reaction under mild conditions in a liquid phase to coat a nanotube with a metal. The nanotube coated with the metal is considered to be applied to an electronic device as a pseudomonodimentional electric conductor and a nanotube coated with a ferromagnetic metal can be utilized as a magnetic material having high performance. The nanotube can be utilized also as a solid catalyst.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]It is related with a carbon nanotube, a metallic coating carbon nanotube which can be used as the intermediate product of a metaled composite material, and a solid catalyst, and a manufacturing method for the same. Application in the field of the electronics which treats the field of industry of the next generation over electronics especially chemicals, a catalyst, metal, and an electron device from chemicals is expected.
[0002]
[Description of the Prior Art]One or more cylinders in which the carbon nanotube rounded off the graphite-like carbon atom side of the number atomic layer of thickness become a nest, and an outer diameter is a very minute substance of nm order. A carbon nanotube is obtained by the arc discharge which used the carbon rod as the electrode, and the extensive synthetic method is known by JP, 6-280116, A and JP, 6-157016, A. A high yield purification method is also developed (the Japanese-Patent-Application-No. No. 153192 [six to] application specification), and use of the comparatively pure carbon nanotube more than a gram order is possible. It has the peculiar shape where a carbon nanotube is hollow where having unique electric physical properties theoretically and the aspect ratio (length / diameter ratio) whose surface area it is minute and is large are large, The application through which it passes industrially as a new carbon material from having the character of the special surface which furthermore originates in shape is expected. However, the easy method of covering the surface of a nanotube by other substances is not learned, but there is no report in particular of art that carries out nanotube covering with metal.
[0003]
[Problem(s) to be Solved by the Invention]As a method of covering a nanotube with metal, a nanotube is soaked in the fused metal, and the method of covering is guessed easily. However, since molten metal has high surface tension, a nanotube cannot be wet but it is clear from the paper (science (Science), Vol. 265, 1850-1852, (1994)) to be a big grain and to be flipped. Generally, since metal is a high-melting point, its a possibility of a chemical reaction occurring if molten metal and a nanotube are contacted, and destroying the structure of a nanotube is high. It is difficult to remove excessive metal other than the covered metal. Thus, the method of using metal directly has some faults.
[0004]The purpose of this invention is to provide the carbon nanotube covered with the metal which did not use metal itself as it was, but was manufactured in the liquid phase and under mild conditions, and its process, in order to avoid such a fault. When it sees from another field, it is making the metal nanowire (quantum wire) which used as the mold the nanotube with the unique shape it being very detailed and long and slender. The carbon nanotube which can be used by this invention as an intermediate product of the composite material of a carbon nanotube, a carbon nanotube, and metal which has a solid catalyst function is obtained.
[0005]
[Means for Solving the Problem]In order to attain the above-mentioned purpose, an invention of the 1st of this invention is a carbon nanotube, wherein the surface is covered with metal. The 2nd invention by carrying out the chemical reaction of a reaction reagent and a carbon nanotube which were chosen from an oxidizer, a nitrating agent, or a sulfonating agent in the liquid phase, A process of producing a carbon nanotube in which a functional group was introduced into said tube surface, It is a manufacturing method of a metallic coating carbon nanotube consisting of a process to which contact a carbon nanotube in which a functional group was introduced in a solution containing metal salt, and an ion exchange reaction, an oxophilic reaction, or a reduction reaction is made to carry out by said functional group.
[0006]This invention deposits ion containing metal as metal or metal salt under a mild condition in the liquid phase using chemical reactions, such as an ion exchange reaction, an oxophilic reaction, and a reduction reaction, and is characterized by covering a nanotube with metal. As metal to cover, they are actinoid represented by uranium (U), a lanthanoids represented by yttrium (Y), a transition metal represented by a ruthenium (Ru) and silver (Ag), and representative element metal represented by tin (Sn).
[0007]
[Function]a carbon nanotube -- the diameter -- number - about ten nm and length are the needle crystals of microscopic graphite of several micrometers.
The aspect ratio is known as a new carbon material with pseudo-one-dimensional structure called hundreds to thousands.
Various uses, such as a catalyst and a structure reinforcement, are devised from the specific structure. Since a nanotube has the unique electric physical properties of changing from a semiconductor to metal depending on the diameter and degree of spiral, the use as an electron device is also considered. In using a nanotube, the character of the surface of a nanotube has an important meaning. When using the nanotube surface as a place of various reactions, a surface chemical state especially has direct influence on a reaction.
[0008]Chemical modification of the wrap graphite side is carried out for the surface of a carbon nanotube, and the manufacturing method of the carbon nanotube which introduced the fundamental functional group is reported by the Japanese-Patent-Application-No. No. 153192 [six to] application specification. By this carrying out the chemical reaction of the reaction reagent and carbon nanotube which were chosen from the oxidizer, the nitrating agent, or the sulfonating agent in the solution layer, and oxidizing a carbon nanotube, Various functional groups, such as a nitro group ($-NO_2$), a sulfone group ($-SO_3H$), a carboxyl group (-COOH), a carbonyl group (>C=O), an ether group (C-O-C), and a phenolic hydroxyl group (-OH), are introduced into a tube surface.

As a reaction reagent, a sulfuric acid, nitric acid, and sulfuric acid-nitric acid mixed solution, a potassium permanganate dilute-sulfuric-acid solution, etc. are used, for example. These surface functional groups have the work make it easy to get wet to a fluid in a nanotube, and make the suspension water solution of a nanotube acidity. Metal covers a carbon nanotube in this invention by performing chemical reactions, such as an ion exchange reaction of the surface functional group of these nanotubes, and the ion containing metal, an oxophilic reaction, and a reduction reaction, in the liquid phase.

[0009]The example of covering of the carbon nanotube using an ion exchange reaction is described. First, the ion (M^+) containing other metal replaces the proton (H^+) of the carboxyl group (NT-COOH) of the surface functional group of a nanotube.

[0010]

$$NT\text{-}COOH+M^+ \rightarrow NT\text{-}COO^- M^+ +H^+ \quad (1)$$

For example, if uranyl acetate ($UO_2(CH_3COO)_2$) is made to act on a nanotube, A proton (H^+) replaces uranyl ion (UO_2^{2+}), and uranyl ion (UO_2^{2+}) is fixed to the nanotube surface. Next, if oxygen in uranyl ion (UO_2^{2+}) is removed by heating or electron beam irradiation, a uranium metal (U) will deposit on the nanotube surface, and a nanotube will be covered with a uranium metal as a result. This reaction does not occur in the nanotube which has not carried out chemical treatments, such as oxidation reaction. This fact shows that existence of the surface functional group of a nanotube is a necessary condition to the ion exchange reaction. Since ionic exchange of the carboxyl group (-COOH) which is a surface functional group of a nanotube can be performed to various positive ions, various nanotubes by which the cation exchange was carried out can be obtained.

[0011]When covering a nanotube with a lanthanoids (Ln), the reaction of all the surface functional groups which exist in a cyclopentadienyl lanthanoids ($Ln(C_5H_5)_{2or3}$) and the nanotube surface is used. In the case of tricyclo pentadienyl yttrium ($Y(C_5H_5)_3$), an oxophilic reaction (oxophilic) is performed to a surface functional group, it decomposes, yttrium (Y) is emitted, and a nanotube is covered. Even if it performs the same reaction to the nanotube in which a surface functional group does not exist, covering by metal is not seen. In this reaction as well as an ion exchange reaction, the surface functional group of a nanotube is required.

[0012]When covering a nanotube with a transition metal, the reduction reaction to zerovalent metal [metal ion / by the aldehyde group (-CHO) which is one of the surface functional groups of a nanotube] is used. For example, in the case of silver (Ag), it is expressed with the following reaction formula (2).

[0013]

$$Ag^+ + -CHO+H_2O \rightarrow Ag^{**} + -COOH+OH^- \quad (2)$$

Before causing the above-mentioned reaction, a nanotube can be covered with more silver (Ag) by pretreating a nanotube with a formaldehyde solution ($HCHO_{aq.}$). The enhancement effect of the deposit silver by pretreatment is considered for the formaldehyde (HCHO) which stuck to the nanotube surface to return a silver ion (Ag^+) to silver (Ag) further. On the other hand, even if it is not oxidizing, i.e., it reacts pretreatment by the reduction reaction and formaldehyde solution ($HCHO_{aq.}$) of a silver ion (Ag^+) to the nanotube in which a functional group does not exist on the surface of a nanotube, covering of the nanotube by silver is not seen. This has a surface functional group of a nanotube indispensable to the reduction reaction from a silver ion (Ag^+) to silver (Ag), and shows that a surface functional group works as the active spot of the nucleation of a silver deposit.

[0014]In the case of the ruthenium (Ru) of platinum group metals, the oxidation-reduction reaction expressed with the following reaction formulae (3) is used.

$$2RuCl_3+3CH_3OH \rightarrow 2Ru^0 {}^{**} + 3HCHO+6HCl \quad (3)$$

[0015]Here, it is returned by methanol (CH_3OH) and ruthenium ion (Ru^{3+}) deposits as a metal ruthenium (Ru^0). However, when a surface functional group exists in a nanotube, it takes place, but covering by this reaction does not take place, when there is no surface functional group. By therefore, the surface functional group (for example, hydroxyl group:-OH) of a nanotube. A possibility that the metal ruthenium (Ru^0) which ruthenium ion (Ru^{3+}) was returned or was returned by methanol by a surface functional group becoming the active spot of the nucleation of metal particles deposited directly is high.

[0016]In the case of the representative element represented by tin (Sn), the reduction reaction expressed with the following reaction formulae (4) is used.

$$Sn^{2+} + 2e^- \rightarrow Sn^{0**} \quad (4)$$

Here, it is returned by the surface functional group of a nanotube, tin ion (Sn^{2+}) deposits as a metal tin, and this covers a nanotube. Since this reaction does not occur in a nanotube without a surface functional group, its surface functional group is indispensable to covering by tin (Sn).

[0017]

[Example]One example of this invention is shown below. In order to investigate the coated state of the sample of the obtained carbon nanotube, it observed by TEM (transmission electron microscope). In order to identify the element of a nanotube coating, the EDX (energy dispersion X-rays micro analysis) spectrum was measured.

[0018](Example 1) Covering **** of the carbon nanotube by uranium (U), Like a statement the carbon nanotube compounded with the carbon arc electric discharge method (JP,6-280116,A, JP,6-157016,A) on the Japanese-Patent-Application-No. No. 153192 [six to] application specifications, By making it react to reagents, such as a sulfuric acid, nitric acid, and sulfuric acid-nitric acid mixed solution and a potassium

permanganate dilute-sulfuric-acid solution, and oxidizing, The carbon nanotube which introduced a functional group like a carboxyl group (-COOH) into the carbon nanotube surface was prepared as a raw material carbon nanotube.

[0019]This raw material nanotube is dipped in the solution of uranyl acetate ($UO_2(CH_3COO)_2$) of about [1 mol/] one concentration. Ultrasonic dispersion is carried out, and if the nanotube to which most reacted precipitates, it will dry under a vacuum after filtration with a glass filter. In order to make a uranium metal (U) **** to a nanotube, heating or the exposure of an electron beam is performed to the sample obtained above.

[0020]The TEM photograph of the sample obtained by this example (covering of the nanotube by uranium (U)) is shown in drawing 1. The TEM photograph of the sample which performed the same processing as Example 1 is shown in drawing 2 to the nanotube which has not carried out chemical treatments, such as oxidation treatment, i.e., a nanotube without a surface functional group, for comparison. Drawing 3 expresses an EDX spectrum and (a) is a spectrum of the nanotube corresponding to drawing 1, and a spectrum over the nanotube corresponding to drawing 2 in (b). With the TEM photograph of drawing 2, covering is not seen to covering being seen on the surface of a nanotube with the TEM photograph of drawing 1. clear from the EDX spectrum of drawing 3 -- as -- the coating of the nanotube of drawing 1 -- uranium (U) -- (-- energy value:about 3.3 keV(s)) is included. When processing shown from the above result in Example 2 to the nanotube by which oxidation treatment was carried out is performed, The proton (H^+) of the carboxyl group (-COOH) of a surface functional group and the ion exchange reaction of uranyl ion (UO_2^{2+}) occurred, and it was checked that the nanotube is covered. If observation of the nanotube of drawing 1 is continued, signs that the coat on the surface changes to many drops will be observed. Drop generation is because uranium (U) in $-COO^- UO_2^{2+}$ generated by ionic exchange on the nanotube surface carried out deposit fusion as metal by electron beam irradiation.

It was checked that a nanotube is covered with uranium (U) as a result.

Other actinoid can be covered with the same method to a nanotube.

[0021](Example 2) The same raw material nanotube as the covering example 1 and cyclopentadienyl lanthanoids ($Y(C_5H_5)_3$) of a nanotube by yttrium (Y) are distributed in dry toluene. In order to except the influence of moisture and oxygen, all operations are performed in the glove box replaced by inert gas. It dissociates from a solution, and the nanotube which reacted is washed and dried with the dry toluene prepared newly.

[0022]The TEM photograph of the nanotube obtained in Example 2 (covering of the nanotube by yttrium (Y)) is shown in drawing 4. The TEM photograph of the sample which performed the same processing as Example 2 is shown in drawing 5 to the nanotube which has not carried out chemical treatments, such as oxidation treatment, i.e., a nanotube without a surface functional group, for comparison. With the TEM photograph of drawing 5, covering is not seen to covering being seen on the surface of a nanotube with the TEM photograph of drawing 4. As for the sample of drawing 5, Y (yttrium) was not detected from measurement of the EDX spectrum at all to Y (yttrium) being detected from the sample of drawing 4. When processing shown in Example 2 from the above result using the nanotube by which oxidation treatment was carried out was performed, the reaction in which a surface functional group participates occurred, and it was checked that the nanotube is covered with Y (yttrium) as a result. Other lanthanoidses can be covered with the same method.

[0023](Example 3) Ultrasonic dispersion of the same raw material nanotube 0.100g as the covering example 1 of the nanotube by silver (Ag) and 4.00 g of the silver nitrate ($AgNO_3$) is carried out to 10 ml of pure water, and suspension is obtained. Next, it is made to boil quietly for 1.5 hours, making this suspension agitate. It filters with cooling and a glass filter to a room temperature after ending reaction, and pure water washes the residue on a filter. Then, vacuum drying is carried out at about 80 **. If a nanotube is processed with a formaldehyde solution ($HCHO_{aq.}$) as pretreatment as above-mentioned, a reduction reaction will be amplified and it will become possible to cover a nanotube with many Ag ultrafine particles.

[0024]The TEM photograph of the nanotube obtained in Example 3 (covering of the nanotube by silver (Ag)) is shown in drawing 6. The TEM photograph of the sample which performed the same processing as Example 3 is shown in drawing 7 to the nanotube which has not carried out chemical treatments, such as oxidation treatment, i.e., a nanotube without a surface functional group, for comparison. The nanotube is not covered with drawing 7 at all to the ultrafine particle of about 5-10 nm in diameter Ag being supported with drawing 6 by the nanotube in the shape of a marshmallow. From the measurement result of the EDX spectrum, the coating was identified silver (Ag). Covering of the nanotube by silver (Ag) was checked from the above result. The metal which can be returned from a metal ion with formaldehyde (HCHO), For example, copper (Cu), nickel (nickel), mercury (Hg), gold (Au), platinum (Pt), (the metal which belongs to a transition element above), bismuth (Bi) (metal belonging to a representative element), etc. can be covered to a nanotube by using the same processing as Example 3.

[0025](Example 4) The suspension to which 50 ml of methanol was made to carry out ultrasonic dispersion of the same raw material nanotube 0.100g as the covering example 1 of the nanotube by a ruthenium (Ru) and 0.500 g of the ruthenium chloride ($RuCl_3 \cdot nH_2O$) is prepared. Next, it flows back at 110 ** under churning of this suspension for 1 hour. cooling to a room temperature after ending reaction, and filtering with a glass filter -- methanol -- subsequently pure water washes. The nanotube covered with the metal which is a residue on a filter is dried at 80 ** under a vacuum. Dry weight is 0.140g and about 10% of all the used rutheniums cover a nanotube.

[0026]The TEM photograph of the nanotube obtained in Example 4 (covering of the nanotube by a ruthenium (Ru)) is shown in drawing 8. The TEM photograph of the sample which performed the same processing as Example 4 is shown in drawing 9 to the nanotube which has not carried out chemical treatments, such as oxidation treatment, i.e., a nanotube without a surface functional group, for comparison. Although the nanotube of drawing 8 is covered by particles several nanometers in diameter, no nanotubes of drawing 9 have adhered. It was identified as a result of EDX that the particles of drawing 8 are rutheniums (Ru). Therefore, it was checked that a nanotube can be covered with a ruthenium (Ru). The platinum group metals (rhodium (Rh), palladium (Pd), male NIUMU (Os), iridium (Ir), platinum (Pt)) in which it is the same method as Example 4, and character resembled the ruthenium (Ru) closely can also be covered to a nanotube.

[0027](Example 5) Concentrated hydrochloric acid (HCl: 36%) of 0.5 ml of covering of the nanotube by tin (Sn) is added to 25 ml of pure water, it acidifies, and 1.00 g of tin chloride ($SnCl_2$) is dissolved in it.

Ultrasonic dispersion of the same raw material nanotube 0.100g as Example 1 is carried out to the above-mentioned tin chloride chloride aqueous acids. When the nanotube to which most reacted precipitates, it filters with a glass filter and is made to dry at 80 ** under a vacuum after washing enough with pure water.
[0028]The TEM photograph of the nanotube obtained in Example 5 (covering of the nanotube by tin (Sn)) is shown in drawing 10. This figure shows that many around 2-nm very fine particles have adhered to the nanotube surface in the diameter. It was identified from measurement of the EDX spectrum that this affix is Sn. As mentioned above, it was checked that it is possible to cover a nanotube with tin (Sn).
[0029]The utilizing method of the nanotube covered with the metal obtained by the above method is described. First, it can use as an intermediate product of the composite material of a nanotube and metal. By covering a nanotube by the method of this invention with metal, the metal that it becomes easy to get used with the composite-ized metal, and a reaction occurs in a nanotube simple substance can also protect it by covering metal. Another metal can also be plated by using an electrochemical process for the nanotube covered with the metal obtained by this invention.
[0030]Next, the use as a solid catalyst is mentioned. In this case, the nanotube itself prevents sintering (melting) of the metal particles which are catalysts, and it has a role of the carrier medium which maintains a high dispersion state. The nanotube covered with the methanation (CH_4) by hydrogen of carbon monoxide (CO) and silver (Ag) can be used for the nanotube covered with the ruthenium (Ru) as catalysts, such as epoxidation (ethyleneoxide) by oxygen of ethylene (C_2H_4). When a nanotube is made to cover other metal, the example of use is given for the following catalyst.
[0031]
(Example of a catalyst)
Pt:$CO+1/2O_2 \rightarrow CO_2$ (perfect combustion of exhaust gas)

Pd:$C_6H_{12} \rightarrow C_6H_6+3H_2$ (refining of gasoline (reforming))

nickel:$C_6H_{12} \rightarrow C_6H_6+3H_2$ (refining of gasoline (reforming))

$CO+3H_2 \rightarrow CH_4+H_2O$ (methanation of carbon monoxide)

Ru:$CO+3H_2 \rightarrow CH_4+H_2O$ (methanation of carbon monoxide)

Fe:$CO+(n/2m)\ H_2 \rightarrow 1/mC_mH_m+H_2O$ (hydrocarbon-izing of carbon monoxide)

Rh:$CO+2H_2 \rightarrow 1/2C_2H_5OH+1/2H_2O$ (methanol-izing of carbon monoxide)

Ir: $C_2H_6+H_2 \rightarrow 2CH_4$ (cracking of hydrocarbon)

[0032]Since it can consider that the nanotube covered with metal is nanowire (quantum wire), it can consider the application to an electron device. If it works as a pseudo-one-dimensional electrical conduction object since it is covered with metal, and also it covers with the metal (Fe, Co, nickel) in which ferromagnetism is shown, it can use as a magnetic material very detailed and long and slender moreover. If a fluid is made to distribute the nanotube covered with this magnetic body, it can use as a magnetic fluid. Although almost spherical metal particles distribute the usual magnetic fluid, since a nanotube has a very large aspect ratio, it is expected that unique magnetism will be shown.
[0033]
[Effect of the Invention]Without destroying the structure of a nanotube, among the liquid phase, under mild conditions, the carbon nanotube surface can be covered with metal and, according to this invention, thereby, it can use as the intermediate product of the composite material of a solid catalyst, and a carbon nanotube and metal, and a magnetic material.

[Translation done.]